

# Enhanced Biogas Production in Anaerobic Digestion of Cassava Wastewater Through Supplementation of Biodiesel Waste as Co-Substrate

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**Abstract-** Anaerobic co-digestion is an attempt to enhance biogas production and improve the economic efficiency of large scale plant operations. In this work, the biodiesel processing waste (BDW) at different portions of 0.5-3.0% (v/v) in feed was subsequently added to an anaerobic hybrid reactor (AHR) treating cassava wastewater (CSW). Enhanced gases production, optimum dosage, digester's performance and stability of each co-digestion conditions were evaluated. The results obtained clearly demonstrated the possible co-digestion of these wastes which increased gases production if BDW did not exceed 2.0%. The supplementation of BDW at 0.5-2.0% can increase 19.4-96.2% and 13.4-56.7% for biogas and methane production, respectively. These daily productions of biogas and methane were 12.6, 13.8, 15.5, 20.7, 18.8, 16.4 L-biogas/d and 8.6, 9.4, 10.3, 13.2, 11.0, 7.7 L-CH<sub>4</sub>/d for 0.5-3.0% BDW addition, compared to 10.6 L-biogas/d and 7.2 L-CH<sub>4</sub>/d of single CSW digestion. Similar gases yields (0.45-0.51 L-biogas/gCOD<sub>removed</sub> and 0.30-0.33 L-CH<sub>4</sub>/gCOD<sub>removed</sub>) and stable performance of AHR were maintained at 0.5-2.0% additions. The optimal dosage which promoted the maximum production was suggested to be 2.0%. Higher BDW dosage was claimed as the limitation. An imbalance digestion was observed as depicted as drop of pH, lower methane composition, and acid accumulation at particularly 3.0% of BDW supplementation.

**Keywords-** Biodiesel waste, biogas, cassava wastewater, co-digestion.

## 1. Introduction

In recent years anaerobic technology has been well established and satisfied performance in organic waste stabilization. Due to the coupling of pollution reduction and energy production, various types of anaerobic digester have been installed and have been operated worldwide including cassava starch production factory in Thailand [1, 2]. However, in case of large-scale biogas plants, the cost-effective portion is sometimes critique. There have many factors that have influenced the long-term profitability, mainly low consistency of biogas production. Such improvement of the process efficiency, the advanced development of production technologies, and application of the near zero-waste disposal strategy results in rather a low amount of waste discarded in many industries. Consequently, the total amount of single waste used as biogas feedstock at a

certain time and in the same place is often insufficient to maintain the consistency of gas production and accomplishes to cost-effectiveness of the plant [3]. To overcome this, the attempts to increase the total gas production by addition of other sources of organic wastes have been investigated [4, 5]. However, most of the previous studies pay much attention to anaerobic co-digestion of lipid rich waste, manure, and agro-wastes [6, 7].

In Thailand biodiesel production has grown rapidly and is considered as a potent source of renewable energy. Not only energy is generated, but also large volumes of wastewater which are used for washing is discharged. This glycerol contaminated constituent is a major by-product accounting for 10-20% of total production [8, 9]. Beside many useful characteristics, such as easy to handle, semi-solid phase, high organic concentration, this crude glycerol contaminated biodiesel wastewater (BDW) is an ideal

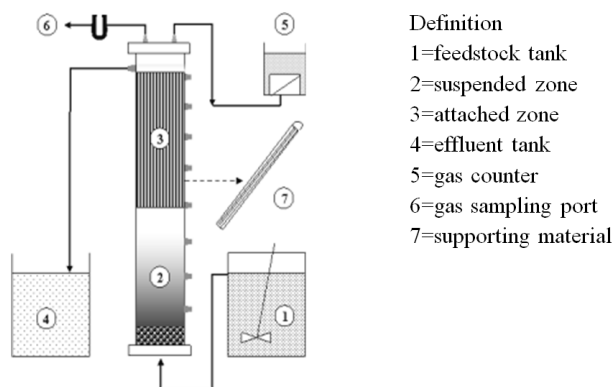
digestible co-substrate for various applications. However, limited information has been found for cassava starch processing wastewater (CSW) co-digestion [9].

Although the addition of other wastes as co-substrate are important to the economic profitability of biogas plants, inadequate information of each waste, i.e. degradability, digestion pattern, toxicity, often leads to the digester's instability [10, 11, 12]. Such optimum conditions and supplemented dose of the co-digestion substrate which have different characteristics are quite difficult to maintain. Moreover, one should be intensively concerned that the additional substrate must not promote any negative effect on the overall performance and stability. Based on different characteristics of wastes, the digestion profile and required time are expected to differ. Therefore, the experiments of each wastes co-digestion should be carefully conducted. In this study, about 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0% (v/v) of BDW was subsequently supplemented to the steady-state maintained digester treating CSW. Optimal BDW dosage, the enhanced gases production potential, process performance and stability were investigated and compared between with and without BDW addition.

## 2. Methodology

### 2.1. Anaerobic Hybrid Reactor

Experiments were conducted in anaerobic hybrid reactor (AHR), a combination schem consists of the suspended and attached growth microbes located in the lower and the upper part, respectively. This made transparent acrylic in cylindrical shape with an effective working volume of 5.5 L and dimensions of 9.4 cm diameter and 86.5 cm high. The attached zone accounted for the upper half part of the digester and used nylon fibre as a supporting material. A gas countering device using water replacement method was connected for daily gas measurement. Influent wastewater was fed continuously in an upward direction without recirculation. Initially, AHR was inoculated with sludge and manure at equal volatile solid (VS) concentration of 5.0 gVS/L or total of 55.0 gVS per reactor. All the experiments were conducted at an ambient condition. In Fig. 1, the schematic configuration of the AHR is shown.



**Fig. 1.** Schematic configuration of anaerobic hybrid reactor used in this study.

### 2.2. Feedstock Characteristics

The principal substrate was CSW collected from a factory located in Chonburi province. To maintain a stable concentration, this raw CSW was partially diluted for 15-25% (v/v) to a certain concentration of 15.0-16.0 gCOD/L. Total alkalinity was added about 1.5 g/L using NaHCO<sub>3</sub>. This wastewater was always kept under 4°C in the controlled temperature refrigerator and used throughout the experiment. For supplemented substrate, BDW was collected from a community-based biodiesel production plant located in Bangkok. This BDW was subsequently added to CSW corresponding to each experimental condition. Chemical characteristics of these raw wastes are summarized in Table 1.

**Table 1.** Characteristics of raw CSW and BDW used in this study

Parameters	CSW	BDW
pH	4.10±0.2	8.01± 0.2
Chemical oxygen demand (g/L)	23.5±3.2	867.6±25.0
Alkalinity (g/L as CaCO <sub>3</sub> )	0.2 ± 0.2	9.8±1.2
Total khjedal nitrogen (g/L)	*nd	0.05±0.001
Total suspended solid (g/L)	5.2±0.1	1.4±0.2
Total volatile acid (g/L as CH <sub>3</sub> COOH)	1.2±0.3	35.2±0.3

\*nd= no data

### 2.3. Experimental Conditions and Analyses

At the beginning, AHR was started up by step increase of organic loading rate (OLR) from 0.5 to targeted OLR at 4.0 kgCOD/m<sup>3</sup>.d. Hydraulic retention time (HRT) was reduced subsequently from 10.0 to 4.0 days. After achieving 4.0 kgCOD/m<sup>3</sup>.d, the digester was maintained for almost 30 days prior to co-digest with BDW. The operational conditions of each supplementation are summarized in Table 2.

In table 2, about six different conditions named orderly from period I to VI, with varied BDW concentrations from 0.5 to 3.0% were conducted. In each condition at least 2 times the HRT was maintained. For analysis of the performance and stability, the regular control parameters such as alkalinity (Alk), pH, chemical oxygen demand (COD), total volatile acid (TVA), were monitored. Alk and TVA were analyzed using titration method while other parameters following the standard procedure (APHA, 1999). Biogas production was measured using the water displacement method. While, methane content was analyzed using gas chromatography (Shimadzu, model GC-9A) equipped with a thermal conductivity detector. Volatile acid composition during each condition was also analyzed using a gas chromatography (Shimadzu, model GC-14b) equipped with a flame ionization detector. The enhanced potential of produced biogases, process efficiency and stability were compared for single substrate digestion and co-digestion.

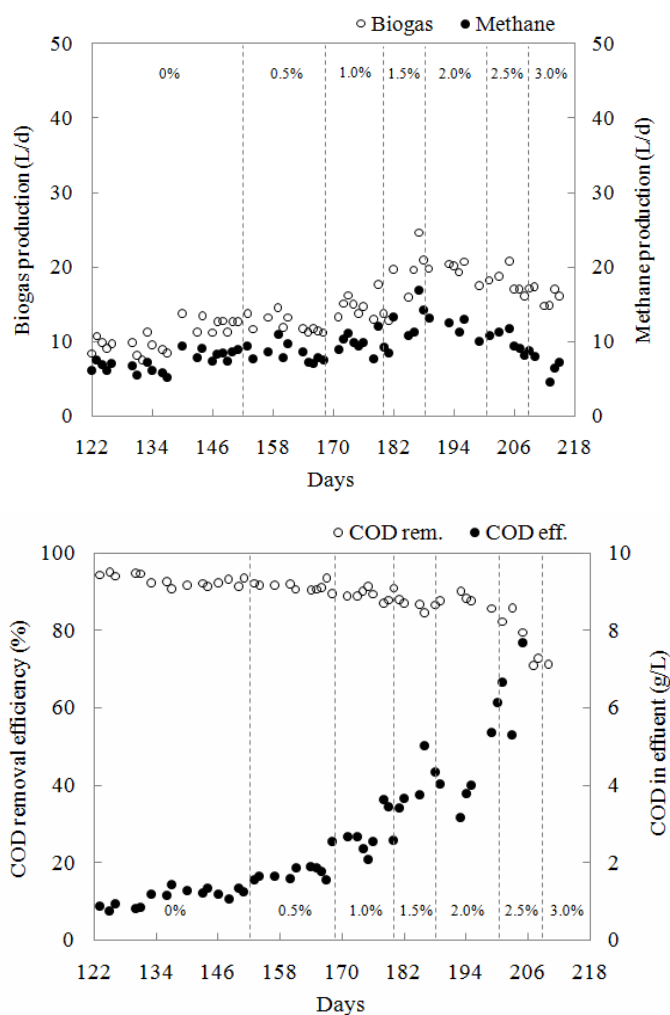
**Table 2.** Experimental conditions

Conditions	Periods						
	0	I	II	III	IV	V	VI
Day	122-150	151-166	167-177	178-185	186-197	198-205	206-215
BDW added* (% v/v)	0%	0.5%	1.0%	1.5%	2.0%	2.5%	3.0%
Influent COD (g/L)	15.8±1.4	20.1±2.8	24.5±2.2	29.0±2.7	32.8±1.7	37.1±1.3	41.4±1.1
HRT (d)	4.0	4.0	4.0	4.0	4.0	4.0	4.0
OLR (kgCOD/m <sup>3</sup> .d)	4.0	5.0	6.0	7.1	8.2	9.4	10.3

\* % by volume per volume of feed

### 3. Results and Discussion

During the start-up, (data not shown), AHR was fed with single substrate of CSW. In this period (0), AHR demonstrated a stable performance which depicted as 93.0±1.4%, 10.6±1.9 L/d, 67.5±3.0% for the COD removal efficiency, averaged daily produced biogas, and its composition, respectively. All the obtained data was performed as a based line condition. In Fig. 2, the performance indicated parameters such as gas produced, COD removal efficiency, and methane content of AHR during the experimented co-digestions are shown.

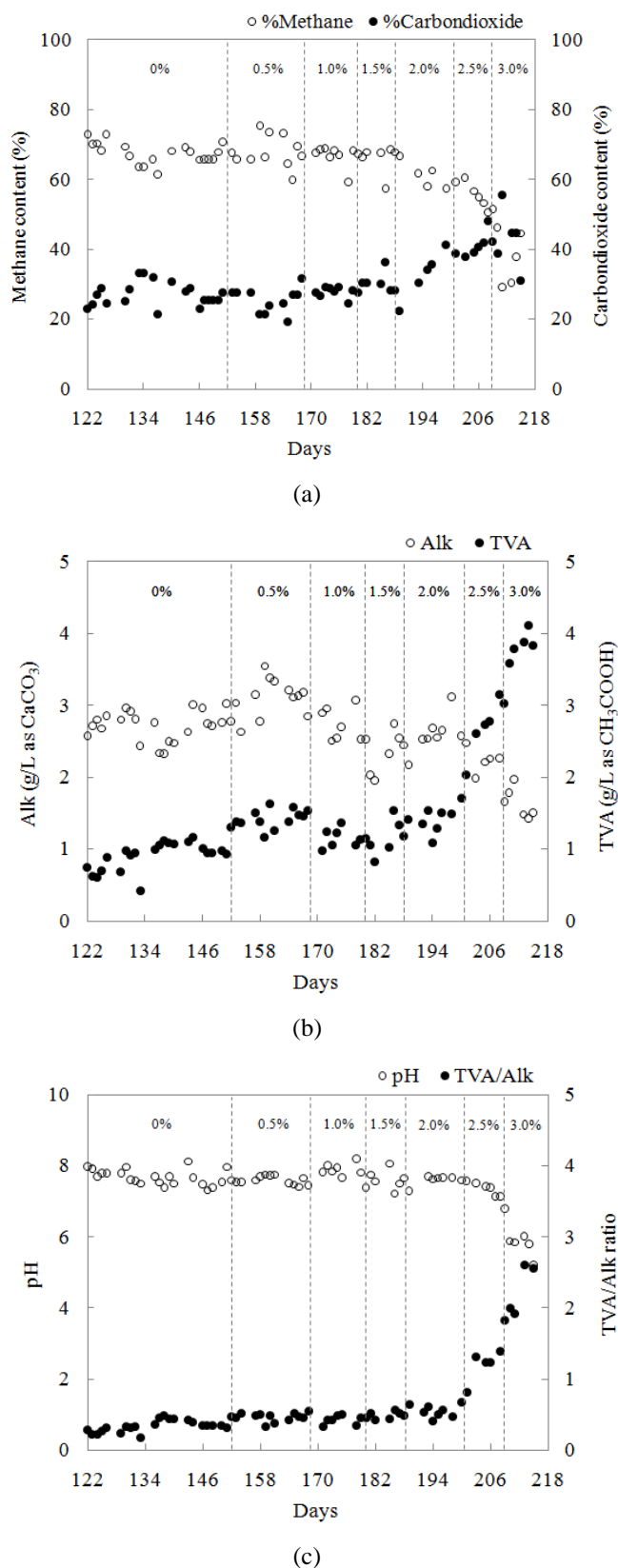


**Fig. 2.** Daily production of biogas and methane (a), COD removal efficiency and effluent COD (b)

Comparing to the based condition (period 0), the biogas production seemed to increase the proportion to an individual dosage increased of BDW. At high concentrations of 2.5 and 3.0% added, a slight lower of produced biogas was observed. These productions were 12.6, 13.8, 15.5, 20.7, 18.8, 16.4 L-biogas/d for 0.5-3.0%, compared to 10.6 L-biogas/d of the normal. The maximum biogas production (96.2%) was achieved at 2.0% BDW supplementation. However, at this condition, the average methane composition was slightly reduced from 66.14-67.46% (period 0-III) to 63.32%. This gradual decrease was obtained when BDW co-digestion exceeded 2.0% concentration, where a sharp decrease of methane composition was clearly observed at 2.5 and 3.0%. Although the higher amount of biogas produced, the methane content was significantly reduced particularly for 2.5% and 3.0% supplemented. This was a sign of the instability which corresponded well with carbon dioxide increasing and the amount of acid accumulated (Fig. 3.).

The addition of BDW about 1.5-2.0% established a more advantageous to anaerobic digestion of CSW. This readily and high digestible waste increased daily biogas production from 10.6 L/d to 15.5-20.7 L/d. This positive effect was also reported by Amon et al. [4]. They found that the addition of 6% crude glycerol to pig manure digestion increased the methane production from 0.57 to 0.68 m<sup>3</sup>/kgVS. While, Fountoulakis et al. [6] suggested that 1% glycerol addition in feed of sewage digestion was optimal dosage which increased methane production about 2.13 times higher than without co-digestion. Moreover, the addition of glycerol at 3% also reported as a limitation which promoted more instability to the digester.

Likewise, the gases production, COD removal efficiency was slightly decreased for 0.5-2.0% co-digestions which were 91.6, 90.3, 88.0, and 87.6%, compared to 93.0, and 83.4 and 71.4% of normal and 2.5-3.0% addition (Fig. 3 and Table 3). This result was apparently due to the excessive amount of substrate from increased BDW in feed. It was worth to note that in CSW digestion a rather short HRT of 4.0 days was maintained. This relatively short time, comparing to previous studies done on manure, may sometime not be enough to have complete digestion of BDW. Thus, the effluent COD concentration corresponded closely with the increase of BDW portions. Moreover, BDW are noted for high impurities containing, i.e. methanol, alkali-salts [9]. These contaminants may have negatively affected the anaerobic digestion process at a high ratio of the supplementation. Similar results were also observed in the co-digestion of manures and glycerol [4, 12] Therefore, in co-digestion of these two wastes, the optimum HRT should be carefully optimized.



**Fig. 3.** Methane and carbondioxide content in produced biogas (a), Alkalinity (Alk) and total volatile acid (TVA) level (b), pH and TVA/Alk ratio (c) of AHR

As well as the increased potential of gases, the digester's stability was also important for biogas plant operations. In Fig. 3, the levels of pH during based condition and 0.5-2.0%

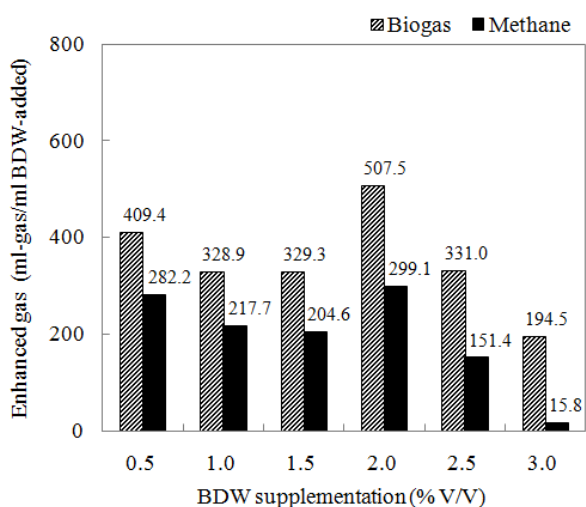
BDW co-digestion was slightly fluctuated between  $7.64 \pm 0.15$ - $7.80 \pm 0.3$ . However, a significant decreased was observed at 3.0% BDW addition. It was dropped down from 7.56 to 6.36 within 5.0 days after supplementation. This was due to a sudden increase of intermediates acids and its accumulation which was increased up to  $3.8 \pm 2.0$  g/L. Corresponded to pH, the system's alkalinity was subsequently reduced from 2.5 to 1.7 g/L with an increase of BDW from 0.5-3.0%. Consequently, TVA/Alk ratio was increased with the increase of BDW. This was due to the fact that BDW contained mostly crude glycerol which is easy to digest. The stable digestion of AHR with this co-digestion was proposed to be maintained if the BDW supplementation did not exceed 2.0%. The instability depicted as high acid accumulation and generated of retarding composition liked propionic and iso-butyric acid were observed at a higher concentration (data not shown) [14]. The work by Holm-Nielsen et al. [15] showed similarly result that the addition of 3-5 g/L of glycerol was easy to digest and increased biogas yields. However, the higher concentration exceeded 5.0-7.0 g/L, the inhibition was observed. The methane was significantly reduced from the organic overloading.

In Table 3, the overall performance of AHR during each experimental condition is shown. These biogas and methane yields of the co-digestion conditions (0.5-2.0%) were not different which were 0.45-0.51 and 0.30-0.33 L-gas/gCOD<sub>removed</sub>. This was similar to 0.53 and 0.34 L-gas/gCOD<sub>removed</sub> of single digestion. The stable yields during these periods reflected that BDW did not promote any negative effect to anaerobes, particularly methanogens. The consisted and high composition of methane in the produced gas was observed. Furthermore, BDW concentrations seemed to be critical to the stable operation of AHR. Influent concentration was corresponded with BDW fractions which were increased from 15.8 to 41.4 gCOD/L. At higher 2%BDW addition, the reactor responded with a sudden increase of VFA, drop of pH and a relatively high concentration of COD in the effluent.

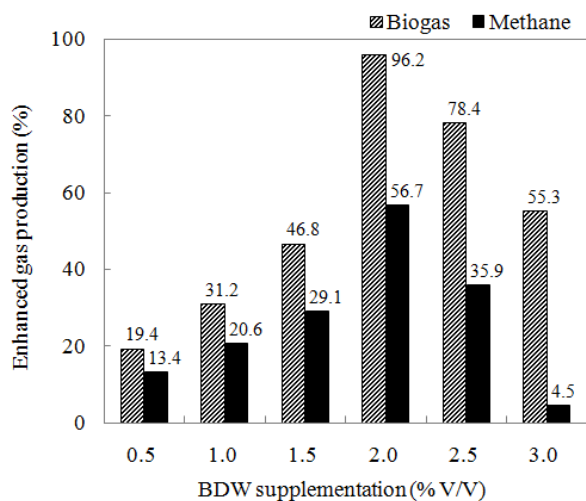
It was worth noting that for each mLof BDW added, the different enhanced biogas production was promoted (Fig. 4). The maximum increase was found at 2.0% BDW which were 507.5 and 299.1 mL-gas/mL-BDW for biogas and methane, respectively. Comparing to previous studied, about 780 to 980 ml-biogas/ml-glycerol was produced during the co-digestion. This was due to the original concentration and organic fraction of each glycerol waste [11, 13]. The increased potential of daily produced gas were 19.4, 31.3, 46.8, 96.2, 78.4, and 55.3% compared to single digestion or equaled to 13.4, 20.6, 24.1, 56.7, 35.9, and 4.5% methane gas increased. In fact, the increased BDW resulted in increases of the organic load. This load did not affect AHR digestion, if it was not over 2.0% concentration. However, in this study, each period was observed for only 2-3 times of HRT. Thus for ensuring the stable performance and stability would be maintained, the longer operational period which maintained optimal co-digestion condition should be investigated.

**Table 3.** Performance of AHR with and without BDW supplementation

Category	Periods						
	0	I	II	III	IV	V	VI
BDW added (% v/v)	0%	0.5%	1.0%	1.5%	2.0%	2.5%	3.0%
COD removal (%)	93.0±1.4	91.6±1.0	90.3±1.7	88.0±1.5	87.6±1.9	83.4±3.0	71.7±1.0
COD <sub>eff.</sub> (g/L)	1.1±0.2	1.7±0.2	2.4±0.4	3.4±0.4	4.1±0.6	6.2±1.4	11.0±1.5
pH	7.67±0.2	7.64±0.2	7.78±0.2	7.80±0.3	7.54±0.2	7.56±0.09	6.36±0.8
Alkalinity (g/L as CaCO <sub>3</sub> )	2.7±0.2	3.1±0.3	2.8±0.2	2.5±0.4	2.5±0.2	2.5±0.3	1.8±0.3
TVA (g/Las CH <sub>3</sub> COOH)	0.9±0.2	1.4±0.2	1.3±0.2	1.0±0.1	1.4±0.2	2.1±0.6	3.5±0.5
Biogas production (L/d)	10.6±1.9	12.6±1.1	13.8±1.8	15.5±2.8	20.7±1.7	18.8±1.4	16.4±1.0
Biogas yield (L/gCOD <sub>removed</sub> )	0.53±0.10	0.49±0.03	0.46±0.06	0.45±0.08	0.51±0.02	0.44±0.05	0.41±0.02
CH <sub>4</sub> content (%)	67.46±3.0	68.31±4.8	67.90±1.1	66.14±3.4	63.32±4.6	58.50±2.2	44.29±9.7
Methane production (L/d)	7.2±1.2	8.6±1.2	9.4±1.2	10.3±2.2	13.2±2.0	11.0±0.7	7.7±1.6
CH <sub>4</sub> yield (L/gCOD <sub>removed</sub> )	0.34±0.09	0.33±0.04	0.31±0.04	0.30±0.07	0.32±0.03	0.26±0.02	0.21±0.02



(a)



(b)

**Fig. 4.** Potential enhancement of daily gas production at various portion of BDW supplementation depicted as per mL-BDW<sub>added</sub> (a), percentage of enhanced gases (b)

#### 4. Conclusion

The result has demonstrated the potential enhancement of biogas when co-digested BDW with CSW in AHR. A stable performance and production of gases were achieved if BDW concentration did not exceed 2.0% (v/v). Daily production increased maximally for 96.2% and 56.7% for biogas and methane at 2.0% BDW addition, respectively. Specific gas productions potential were 194.5-507.5 mL-biogas/mL-BDW and 15.8-299.1 mL-CH<sub>4</sub>/mL-BDW added. The suggested dosage of BDW to anaerobic co-digestion of CSW was 2.0%. BDW with a concentration ratio which exceeded 2.0% seemed to promote more instability which clearly depicted as acid accumulation, drop of pH, and low quality of produced gas and the effluent. According to this result, there is a potential application of BDW as a co-substrate for anaerobic digestion of CSW which regarded to enhance its gas production. Not only daily produced gas is increased, but also improves of plant's profitability and alternatively utilized of BDW.

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